Improved H_2 Storage in Zeolitic Imidazolate Frameworks (ZIFs) Using Li^+, Na^+, and K^+ Dopants, with an Emphasis on Delivery H_2 Uptake

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Supporting Information

S.1 Quantum mechanical calculations on the binding energies of Li^+, Na^+, and K^+ ions to the imidazolate linkers

In this work, we considered the doping of alkali metal cations (Li^+, Na^+, and K^+) to zeolitic-imidazolate frameworks (ZIFs) to improve H_2 uptake at ambient temperature. To build structures of the alkali metal-doped ZIFs, we need to find positions of the alkali-metal cations in the ZIFs. In this work, the binding energies of the alkali-metal cations to the imidazolate linkers were calculated by MP2 (second-order Møller-Plesset) *ab-initio* calculations to investigate the sites where the metal dopants absorb onto the linkers. The binding energies were calculated the following equation:

$$E_{bind}(\text{M-IM}) = E_{tot}(\text{M-IM}) - E_{tot}(M^+) - E_{tot}(IM^-) \qquad (1)$$

Where E_{tot}(M-IM) indicates the total energy of neutral M-IM complex, $E_{tot}(M^+)$ indicates that of isolated metal cation (M^+), and $E_{tot}(IM^-)$ indicates that of isolated imidazolate linkers (IM^-). These MP2 calculations were performed with the Q-CHEM[S1] software. The results are summarized in Table S1.

In addition, we calculated the energy change (ΔE) by the MP2 method for the following reaction:

$$\text{IM-H} + 1/2\text{M(crystal)} \rightarrow \text{M-IM} + 1/2H_2 \qquad (2)$$

And, the ΔE is calculated by the equation (3):

$$\Delta E = E_{tot}(\text{M-IM}) + 1/2\ E_{tot}(H_2) - E_{tot}(\text{IM-H}) - 1/2E_{tot}(M_{crystal}) \qquad (3)$$

where E_{tot}(M-IM) indicates the total energy of neutral M-IM complex, $E_{tot}(H_2)$ is that of H2 molecule, E_{tot}(IM-H) indicates that of neutral imidazole system, and $E_{tot}(M_{crystal})$ indicates that of crystalline alkali metal (M) with a body-centered cubic crystal structure.

For calculating the $E_{tot}(M_{crystal})$, we considered the following equation:

$$E_{coh}(M) = 1/2E_{tot}(M_{crystal}) - E_{tot}(M_{atom}) \qquad (4)$$

Here, E_{coh}(M) indicates the cohesive energies of crystalline metals which are from experiment values (37.70 kcal/mol for Li crystal, 25.67 kcal/mol for Na crystal, and 21.54 kcal/mol for K crystal).[S2] And, $E_{tot}(M_{atom})$ indicates the MP2 total energy of an metal (M) atom.

The calculated ΔE is summarized in Table S2.

Table S1. The binding energies (kcal/mol) of Li^+, Na^+, and K^+ to the 6 imidazolate linkers calculated by the MP2/G3MP2LARGE method.

Dopant	IM^- ($C_3N_2H_3^-$)	nIM^- ($C_3N_3O_2H_2^-$)	bIM^- ($C_7N_2H_5^-$)	$mbIM^-$ ($C_8N_2H_7^-$)	$cbIM^-$ ($C_7N_2ClH_4^-$)	$nbIM^-$ ($C_7N_3O_2H_4^-$)
Li^+	-151.77	-130.02	-139.33[a]	-140.10[a]	-133.49[a]	-125.12[a]
			-135.15[b]	-135.71[b]	-127.65[b]	-118.82[b]
Na^+	-125.94	-108.11	-116.97[a]	-117.44[a]	-111.78[a]	-57.71[a]
			-113.56[b]	Unstable[c]	Unstable[c]	Unstable[c]
K^+	-54.66	-36.51	-57.94[a]	-58.78[a]	-56.67[a]	-33.70[a]
			Unstable[c]	Unstable[c]	Unstable[c]	Unstable[c]

[a] On the 5-membered ring, [b] On the 6-membered ring, [c] Unstable on the 6-membered ring, instead the alkali metal ions move on the 5-membered ring.

Table S2. The binding energies, ΔE (kcal/mol) for formation of M-IM complexes calculated by the MP2/G3MP2LARGE method.

Dopant	IM^- ($C_3N_2H_3^-$)	nIM^- ($C_3N_3O_2H_2^-$)	bIM^- ($C_7N_2H_5^-$)	$mbIM^-$ ($C_8N_2H_7^-$)	$cbIM^-$ ($C_7N_2ClH_4^-$)	$nbIM^-$ ($C_7N_3O_2H_4^-$)
Li^+	-45.22	-44.10	-42.07[a]	-42.01[a]	-42.30[a]	-42.60[a]
			-37.88[b]	-37.62[b]	-36.46[b]	-36.30[b]
Na^+	2.07	-0.72	1.75[a]	2.12[a]	0.87[a]	46.28[a]
			5.16[b]	Unstable[c]	Unstable[c]	Unstable[c]
K^+	47.48	45.01	34.93[a]	34.92[a]	30.12[a]	44.42[a]
			Unstable[c]	Unstable[c]	Unstable[c]	Unstable[c]

[a] On the 5-membered ring, [b] On the 6-membered ring, [c] Unstable on the 6-membered ring, instead the alkali metal ions move on the 5-membered ring.

S.2 Development of the force field (FF) from quantum mechanical calculations

We used MP2 calculations to determine interaction potential of H_2 with imidazolate organic linkers, Zn metallic joints of the ZIFs, and alkali metal cations (Li^+, Na^+, and K^+). Then we fitted these results to obtain Morse pair potentials (Eq. 2) between each atom of H_2 and ZIF.

$$U_{ij}(r_{ij}) = D\left\{\exp[\alpha(1-\frac{r_{ij}}{r_o})] - 2\cdot\exp[\frac{\alpha}{2}(1-\frac{r_{ij}}{r_o})]\right\} \quad (2)$$

Here the parameter D is the well depth, r_o is the equilibrium bond distance, and α determines the stiffness (force constant).

In the GCMC simulation for simulation of H_2 uptake in alkali metal-doped ZIFs, we need 12 FFs to describe non-bonded interactions of H_2---H_2 and H_2---ZIFs such as H_A---H_A, H_A---C_R, H_A---C_3, H_A---H_, H_A---N_{IM}, H_A---N_{NO2}, H_A---O, H_A---Cl, H_A---Zn, H_A---Li, H_A---Na, and H_A---K where H_A means a hydrogen atom in a H_2 molecule, C_R does an aromatic carbon atom, C_3 does a sp^3 carbon, and H_ does a hydrogen atom bonded to the aromatic carbon, N_{IM} does an nitrogen atom in an imdazolate linker, N_{NO2} does an nitrogen atom in a functional group (-NO_2), O does an oxygen atom in a functional group (-NO_2), Cl does a chlorine atom in a functional group (-C_6H_5Cl), Zn does a zinc atom in a ZnN_4 metallic joint part, and Li, Na, and K do alkali metal dopants in ZIFs. We previously developed FFs for H_2---ZIF, and then reproduced experimental H_2 isotherms of the ZIF-8 with the developed FFs:[S3] the result is also shown in Fig. S1. Thus of the 12 FFs to simulate H_2 uptake in alkali metal-doped ZIFs, the first 9 FFs (H_A---H_A, H_A---C_R, H_A---C_3, H_A---H_, H_A---N_{IM}, H_A---N_{NO2}, H_A---O, H_A---Cl, and H_A---Zn) could be used with ones developed in the previous works.[S3]

For the H_A---Li, H_A---Na, and H_A---K FFs, we carried out CCSD(T)/G3MP2LARGE calculations for the interaction between H_2 and alkali metal ions, shown in Fig. S2. The *ab-initio* calculations indicate that the H_2 binding energies to alkali-metal ions are 5.61 kcal/mol for Li^+, 2.92 kcal/mol for Na^+, and 1.29 kcal/mol for K^+, which are very close to the FF results: 5.62 kcal/mol for Li^+, 2.71 kcal/mol for Na^+, and 1.28 kcal/mol for K^+. These calculations were performed with the Q-CHEM[S1] software.

All of the FFs used in this work are summarized in Table S3.

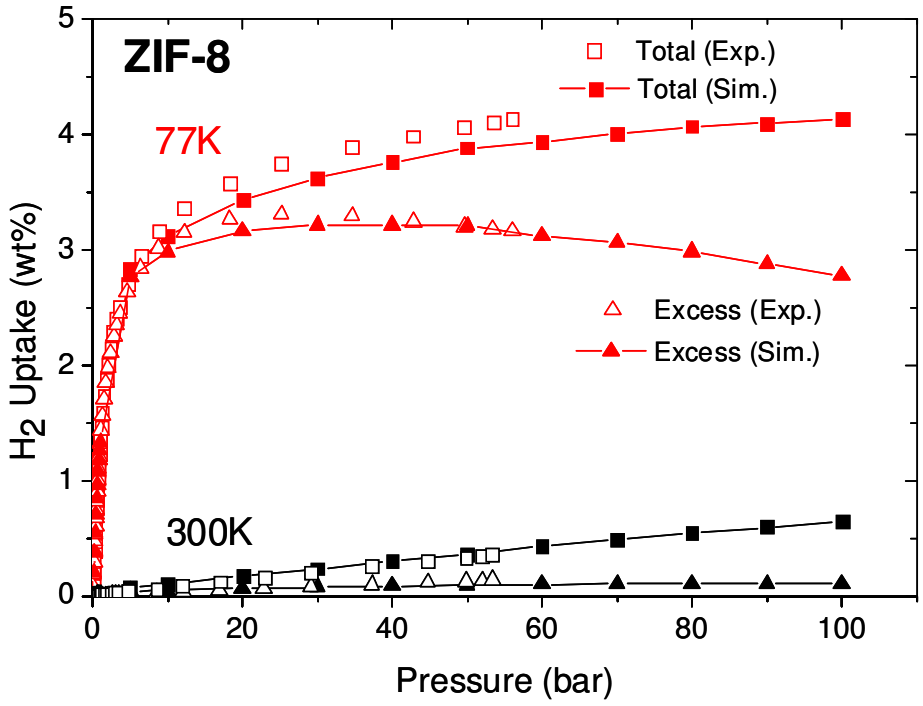

Figure S1. Comparison of simulated (solid) and experimental (open) H_2 adsorption isotherms of ZIF-8 at 77 (red) and 300 K (black).

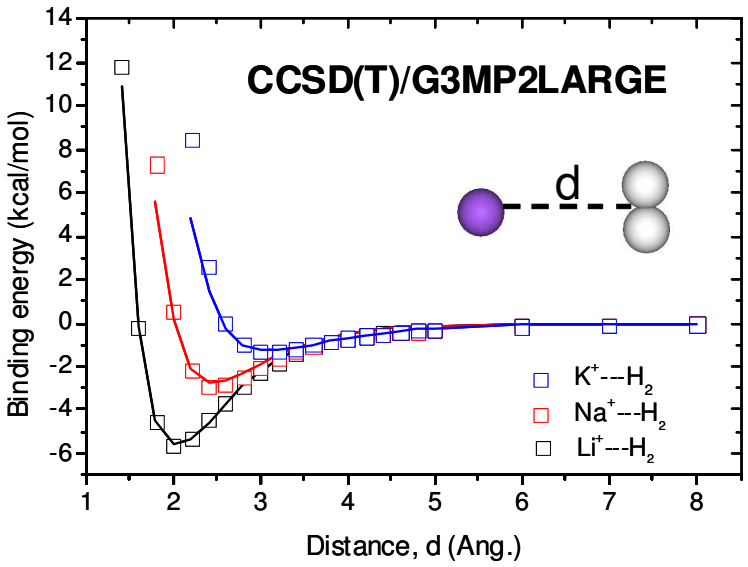

Figure S2. Comparison of the quantum calculations (CCSD(T)/G3MP2LARGE) and fitted force fields for H_2 interacting with Li^+, Na^+, and K^+. Here the square symbol indicates the CCSD(T) results, and the line indicates the fitted FFs.

Table S3. van der Waals FF parameters used in the GCMC simulations.

Term	D (kcal/mol)	r_0 (Å)	γ [a]
C_R---H_A	0.10082	3.12022	12.00625
H_---H_A	0.00087	3.24722	12.00625
H_A---H_A	0.01815	3.56980	10.70940
C_3---H_A	0.05239	3.02401	14.90625
N_{IM}---H_A	0.06300	3.30170	11.62254
N_{NO2}---H_A	0.07156	3.09389	10.29909
O_{NO2}---H_A	0.08482	3.63895	9.76998
Cl---H_A	0.15735	3.46095	13.90551
Zn---H_A	0.08067	3.53954	11.94487
Li---H_A	2.82251	2.07130	6.63828
Na---H_A	1.36865	2.48878	7.71053
K---H_A	0.64825	3.12789	8.03525

[a] $\gamma=2r_0\alpha$. In the Cerius2 software, the γ is used as a default value in the FF file.

S.3 Simulated H_2 uptake capacities (at 243, 274, and 298 K) of all alkali metal-doped ZIFs considered in this work

Li-ZIF-68									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	2.153	2.149	7.832	1.871	1.868	7.939	1.597	1.594	8.034
5	2.420	2.402	7.521	2.199	2.183	7.680	2.010	1.995	7.757
10	2.565	2.530	7.340	2.319	2.287	7.523	2.162	2.131	7.594
20	2.756	2.688	7.098	2.508	2.444	7.269	2.339	2.278	7.380
30	2.869	2.766	6.930	2.630	2.535	7.126	2.433	2.342	7.243
40	2.981	2.844	6.815	2.691	2.564	7.011	2.515	2.394	7.133
50	3.029	2.859	6.694	2.808	2.649	6.890	2.630	2.479	7.010
60	3.149	2.945	6.590	2.888	2.697	6.781	2.664	2.484	6.918
70	3.187	2.949	6.511	2.932	2.710	6.722	2.742	2.532	6.843
80	3.230	2.958	6.469	2.969	2.716	6.657	2.807	2.567	6.783
90	3.268	2.962	6.406	3.012	2.726	6.592	2.873	2.602	6.749
100	3.308	2.968	6.346	3.096	2.780	6.518	2.929	2.628	6.659

Na-ZIF-68									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	0.800	0.797	5.232	0.500	0.497	5.386	0.339	0.337	5.495
5	1.321	1.305	4.907	0.991	0.977	4.999	0.753	0.739	5.070
10	1.567	1.536	4.776	1.244	1.215	4.851	0.995	0.968	4.898
20	1.804	1.742	4.640	1.492	1.435	4.699	1.266	1.212	4.743
30	1.933	1.840	4.549	1.648	1.563	4.615	1.430	1.348	4.659
40	2.061	1.937	4.487	1.764	1.650	4.547	1.552	1.445	4.589
50	2.131	1.977	4.390	1.859	1.717	4.487	1.636	1.501	4.514
60	2.205	2.021	4.370	1.923	1.753	4.433	1.716	1.554	4.477
70	2.279	2.064	4.336	2.000	1.802	4.392	1.787	1.599	4.439
80	2.324	2.079	4.292	2.054	1.828	4.367	1.843	1.628	4.395
90	2.361	2.085	4.258	2.099	1.845	4.320	1.881	1.639	4.367
100	2.406	2.099	4.224	2.145	1.863	4.295	1.944	1.676	4.346

K-ZIF-68									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	0.346	0.344	4.214	0.207	0.205	4.312	0.133	0.130	4.324
5	0.746	0.733	3.888	0.514	0.502	3.97	0.381	0.369	4.046
10	0.978	0.952	3.766	0.714	0.690	3.842	0.555	0.532	3.909
20	1.237	1.185	3.647	0.953	0.905	3.708	0.775	0.729	3.766
30	1.402	1.324	3.577	1.116	1.044	3.639	0.922	0.854	3.678
40	1.521	1.418	3.532	1.230	1.134	3.577	1.041	0.951	3.624
50	1.613	1.484	3.495	1.326	1.206	3.540	1.128	1.015	3.583
60	1.682	1.528	3.460	1.412	1.269	3.510	1.217	1.081	3.550
70	1.754	1.575	3.438	1.471	1.304	3.480	1.276	1.118	3.511
80	1.806	1.601	3.412	1.538	1.348	3.465	1.341	1.161	3.497
90	1.850	1.620	3.393	1.586	1.372	3.436	1.390	1.187	3.469
100	1.910	1.654	3.380	1.625	1.388	3.416	1.430	1.205	3.446

Li-ZIF-69									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	1.812	1.810	8.116	1.563	1.561	8.255	1.363	1.361	8.411
5	2.082	2.074	7.761	1.889	1.881	7.933	1.688	1.680	8.041
10	2.207	2.190	7.561	2.000	1.983	7.756	1.850	1.834	7.863
20	2.346	2.311	7.334	2.166	2.133	7.511	2.015	1.983	7.632
30	2.439	2.387	7.161	2.261	2.211	7.341	2.099	2.051	7.450
40	2.530	2.460	7.014	2.314	2.248	7.216	2.183	2.120	7.350
50	2.582	2.495	6.909	2.392	2.309	7.102	2.237	2.158	7.256
60	2.628	2.524	6.825	2.416	2.317	7.054	2.288	2.194	7.172
70	2.681	2.559	6.722	2.487	2.371	6.956	2.308	2.197	7.086
80	2.726	2.587	6.655	2.525	2.393	6.859	2.383	2.257	7.004
90	2.758	2.602	6.617	2.553	2.404	6.835	2.420	2.278	6.956
100	2.804	2.630	6.547	2.611	2.446	6.768	2.462	2.304	6.905

Na-ZIF-69									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	0.610	0.609	5.131	0.373	0.371	5.226	0.239	0.238	5.250
5	1.036	1.028	4.864	0.766	0.758	4.925	0.579	0.572	4.962
10	1.211	1.195	4.729	0.964	0.949	4.810	0.764	0.749	4.841
20	1.399	1.367	4.589	1.152	1.122	4.665	0.976	0.947	4.696
30	1.524	1.476	4.507	1.289	1.243	4.573	1.106	1.063	4.612
40	1.612	1.548	4.425	1.372	1.312	4.495	1.197	1.140	4.544
50	1.680	1.600	4.369	1.441	1.365	4.430	1.270	1.199	4.481
60	1.729	1.633	4.311	1.506	1.416	4.399	1.335	1.249	4.450
70	1.781	1.669	4.288	1.558	1.453	4.359	1.389	1.289	4.413
80	1.824	1.697	4.243	1.604	1.484	4.325	1.430	1.316	4.365
90	1.875	1.731	4.217	1.636	1.502	4.287	1.469	1.341	4.334
100	1.906	1.746	4.188	1.683	1.533	4.260	1.513	1.371	4.308

K-ZIF-69									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	0.265	0.264	4.162	0.150	0.149	4.240	0.093	0.092	4.249
5	0.610	0.603	3.908	0.409	0.403	3.971	0.293	0.287	4.020
10	0.808	0.795	3.812	0.580	0.567	3.867	0.442	0.430	3.905
20	1.021	0.994	3.713	0.782	0.757	3.756	0.623	0.599	3.795
30	1.147	1.107	3.657	0.911	0.873	3.695	0.747	0.712	3.724
40	1.242	1.189	3.618	1.004	0.954	3.656	0.837	0.789	3.684
50	1.321	1.255	3.584	1.079	1.017	3.614	0.924	0.864	3.622
60	1.371	1.291	3.559	1.146	1.072	3.588	0.976	0.905	3.611
70	1.421	1.329	3.531	1.195	1.108	3.559	1.028	0.945	3.587
80	1.466	1.360	3.510	1.245	1.146	3.539	1.084	0.989	3.576
90	1.501	1.382	3.489	1.284	1.173	3.527	1.117	1.010	3.553
100	1.535	1.403	3.470	1.316	1.192	3.504	1.154	1.036	3.531

Li-ZIF-70									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	2.120	2.114	7.673	1.756	1.750	7.927	1.445	1.440	8.176
5	2.495	2.464	7.238	2.237	2.208	7.407	2.004	1.977	7.562
10	2.669	2.608	7.018	2.442	2.385	7.178	2.227	2.173	7.320
20	2.867	2.745	6.743	2.647	2.534	6.892	2.452	2.344	7.035
30	2.992	2.809	6.552	2.781	2.611	6.735	2.602	2.442	6.851
40	3.112	2.869	6.413	2.892	2.666	6.591	2.716	2.503	6.706
50	3.208	2.904	6.289	2.985	2.704	6.473	2.788	2.521	6.602
60	3.273	2.909	6.197	3.040	2.702	6.388	2.866	2.546	6.486
70	3.337	2.912	6.121	3.099	2.705	6.285	2.939	2.567	6.416
80	3.402	2.917	6.035	3.166	2.716	6.201	3.005	2.579	6.338
90	3.451	2.906	5.973	3.221	2.714	6.146	3.055	2.577	6.276
100	3.504	2.899	5.907	3.275	2.714	6.088	3.077	2.546	6.198

Na-ZIF-70									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	0.826	0.820	5.273	0.559	0.554	5.406	0.394	0.389	5.455
5	1.362	1.335	4.792	1.022	0.997	4.922	0.818	0.794	5.021
10	1.645	1.591	4.606	1.301	1.251	4.712	1.062	1.015	4.792
20	1.950	1.842	4.416	1.588	1.488	4.497	1.345	1.251	4.562
30	2.141	1.980	4.309	1.794	1.645	4.374	1.546	1.405	4.432
40	2.273	2.059	4.229	1.933	1.735	4.279	1.682	1.494	4.340
50	2.394	2.128	4.160	2.051	1.804	4.209	1.804	1.570	4.268
60	2.480	2.160	4.114	2.142	1.846	4.158	1.908	1.628	4.212
70	2.567	2.195	4.065	2.235	1.890	4.109	1.983	1.657	4.151
80	2.628	2.203	4.013	2.288	1.894	4.080	2.033	1.660	4.107
90	2.693	2.215	3.985	2.370	1.928	4.011	2.122	1.703	4.075
100	2.745	2.215	3.956	2.441	1.949	4.004	2.191	1.725	4.037

K-ZIF-70									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	0.302	0.298	3.768	0.177	0.173	3.853	0.114	0.110	3.867
5	0.755	0.733	3.462	0.510	0.490	3.540	0.373	0.354	3.590
10	1.023	0.979	3.343	0.750	0.709	3.404	0.574	0.536	3.455
20	1.340	1.252	3.211	1.036	0.955	3.288	0.844	0.767	3.332
30	1.518	1.386	3.172	1.227	1.106	3.227	1.019	0.904	3.258
40	1.654	1.479	3.125	1.370	1.208	3.172	1.155	1.002	3.212
50	1.771	1.552	3.094	1.470	1.268	3.142	1.270	1.079	3.173
60	1.847	1.586	3.062	1.563	1.320	3.112	1.356	1.128	3.146
70	1.928	1.623	3.038	1.644	1.361	3.080	1.427	1.161	3.114
80	1.997	1.648	3.013	1.712	1.390	3.063	1.507	1.203	3.098
90	2.062	1.670	2.999	1.773	1.410	3.040	1.576	1.234	3.073
100	2.112	1.677	2.975	1.830	1.428	3.023	1.622	1.242	3.051

Li-ZIF-78									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	1.650	1.648	8.205	1.447	1.446	8.359	1.276	1.275	8.465
5	1.857	1.851	7.818	1.671	1.665	8.025	1.555	1.549	8.108
10	1.958	1.946	7.617	1.795	1.784	7.806	1.661	1.651	7.941
20	2.172	2.148	7.244	1.947	1.925	7.532	1.801	1.780	7.692
30	2.267	2.232	7.092	2.054	2.021	7.332	1.887	1.854	7.503
40	2.374	2.327	6.901	2.140	2.095	7.146	1.981	1.938	7.348
50	2.454	2.396	6.782	2.218	2.163	7.048	2.036	1.982	7.242
60	2.501	2.431	6.705	2.263	2.197	6.951	2.084	2.021	7.141
70	2.556	2.475	6.622	2.306	2.228	6.868	2.143	2.068	7.027
80	2.604	2.511	6.555	2.368	2.279	6.786	2.200	2.114	6.965
90	2.643	2.539	6.479	2.405	2.306	6.728	2.214	2.117	6.915
100	2.689	2.574	6.412	2.464	2.353	6.651	2.274	2.167	6.834

Na-ZIF-78									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	0.654	0.653	5.277	0.408	0.407	5.351	0.260	0.259	5.358
5	1.018	1.013	5.038	0.780	0.775	5.092	0.600	0.595	5.115
10	1.174	1.163	4.889	0.955	0.945	4.957	0.774	0.765	4.999
20	1.336	1.314	4.734	1.133	1.113	4.815	0.970	0.951	4.866
30	1.438	1.406	4.616	1.243	1.212	4.715	1.083	1.054	4.745
40	1.503	1.460	4.547	1.322	1.282	4.642	1.168	1.129	4.685
50	1.577	1.524	4.476	1.373	1.322	4.570	1.230	1.181	4.632
60	1.616	1.552	4.411	1.426	1.365	4.525	1.292	1.234	4.580
70	1.660	1.585	4.378	1.474	1.403	4.469	1.330	1.261	4.530
80	1.698	1.614	4.334	1.522	1.441	4.427	1.376	1.298	4.495
90	1.730	1.635	4.293	1.538	1.447	4.391	1.408	1.320	4.463
100	1.772	1.666	4.266	1.586	1.485	4.374	1.451	1.353	4.429

K-ZIF-78									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	0.298	0.297	4.333	0.170	0.169	4.246	0.107	0.106	4.406
5	0.620	0.615	4.062	0.433	0.429	4.136	0.316	0.311	4.190
10	0.799	0.790	3.936	0.591	0.582	4.012	0.457	0.448	4.064
20	0.988	0.970	3.813	0.778	0.760	3.890	0.632	0.615	3.938
30	1.100	1.074	3.747	0.892	0.866	3.817	0.745	0.719	3.858
40	1.172	1.137	3.697	0.978	0.943	3.753	0.823	0.789	3.796
50	1.244	1.199	3.651	1.045	1.001	3.723	0.899	0.857	3.766
60	1.301	1.247	3.618	1.103	1.051	3.688	0.952	0.901	3.726
70	1.332	1.270	3.594	1.156	1.096	3.659	1.003	0.944	3.699
80	1.385	1.314	3.566	1.194	1.125	3.629	1.044	0.977	3.670
90	1.408	1.327	3.549	1.217	1.139	3.595	1.079	1.004	3.639
100	1.449	1.360	3.522	1.259	1.172	3.586	1.117	1.033	3.630

Li-ZIF-79									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	2.026	2.023	8.050	1.748	1.745	8.175	1.472	1.469	8.343
5	2.233	2.219	7.812	2.067	2.054	7.904	1.894	1.881	7.979
10	2.335	2.307	7.645	2.172	2.146	7.742	2.026	2.001	7.818
20	2.463	2.407	7.411	2.310	2.257	7.551	2.171	2.122	7.642
30	2.554	2.470	7.243	2.385	2.306	7.410	2.271	2.197	7.497
40	2.627	2.515	7.120	2.469	2.364	7.289	2.334	2.235	7.406
50	2.691	2.551	7.001	2.523	2.391	7.190	2.382	2.258	7.309
60	2.747	2.580	6.927	2.560	2.403	7.107	2.443	2.294	7.226
70	2.792	2.597	6.834	2.626	2.443	7.026	2.484	2.311	7.133
80	2.828	2.605	6.769	2.657	2.447	6.973	2.522	2.324	7.067
90	2.886	2.636	6.687	2.700	2.465	6.894	2.565	2.343	7.013
100	2.926	2.648	6.617	2.717	2.456	6.844	2.584	2.337	6.959

Na-ZIF-79									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	0.651	0.649	5.083	0.382	0.380	5.103	0.238	0.236	5.087
5	1.101	1.090	4.836	0.818	0.807	4.893	0.607	0.596	4.888
10	1.310	1.288	4.724	1.027	1.004	4.769	0.814	0.791	4.778
20	1.502	1.458	4.582	1.261	1.217	4.639	1.048	1.003	4.660
30	1.628	1.561	4.493	1.376	1.310	4.550	1.181	1.114	4.572
40	1.725	1.637	4.426	1.475	1.386	4.480	1.280	1.191	4.506
50	1.794	1.683	4.361	1.562	1.452	4.421	1.366	1.255	4.454
60	1.869	1.737	4.324	1.619	1.486	4.382	1.426	1.292	4.402
70	1.934	1.780	4.265	1.671	1.517	4.331	1.494	1.338	4.364
80	1.974	1.798	4.243	1.720	1.543	4.287	1.549	1.371	4.330
90	2.022	1.824	4.204	1.760	1.562	4.262	1.589	1.389	4.303
100	2.042	1.822	4.164	1.819	1.599	4.199	1.644	1.422	4.276

K-ZIF-79									
	243 K			273 K			298 K		
Pressure (bar)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)	Total (wt%)	Excess (wt%)	Q_{st} (kcal/mol)
1	0.258	0.256	4.112	0.144	0.142	4.190	0.094	0.092	4.216
5	0.595	0.584	3.820	0.398	0.388	3.885	0.291	0.281	3.943
10	0.788	0.766	3.692	0.572	0.551	3.761	0.431	0.412	3.808
20	1.017	0.974	3.579	0.781	0.741	3.629	0.621	0.583	3.674
30	1.151	1.086	3.508	0.921	0.861	3.561	0.748	0.691	3.597
40	1.251	1.165	3.453	1.016	0.937	3.513	0.855	0.779	3.543
50	1.331	1.223	3.418	1.091	0.992	3.464	0.927	0.832	3.497
60	1.397	1.268	3.387	1.155	1.036	3.428	0.998	0.885	3.467
70	1.448	1.297	3.353	1.219	1.081	3.404	1.052	0.920	3.430
80	1.504	1.332	3.336	1.268	1.109	3.374	1.099	0.948	3.407
90	1.564	1.370	3.292	1.321	1.143	3.340	1.149	0.980	3.389
100	1.578	1.363	3.293	1.363	1.165	3.345	1.192	1.003	3.369

S.4 H_2 clouds in Li-ZIF-70, Na-ZIF-70, K-ZIF-70, and ZIF-70

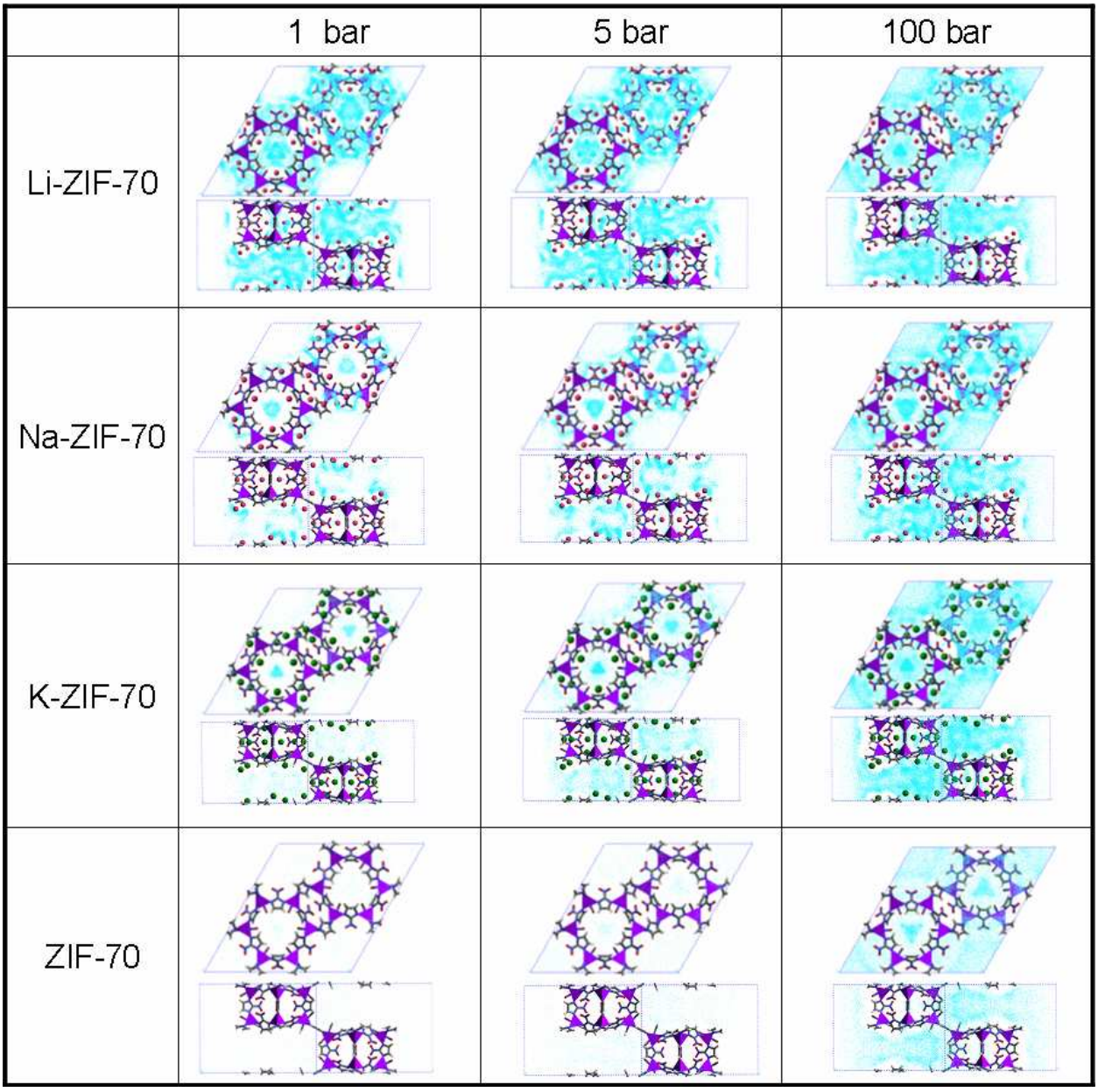

Figure S3. The ensemble average (cyan color) from the GCMC simulation for H_2 uptake in Li-ZIF-70, Na-ZIF-70, and K-ZIF-70 at 1, 5, and 100 bar, in which pristine ZIF-70 is also included for comparison. For each pressure, top and bottom snapshots are top-view and side-view, respectively.

S.5 Comparison of delivery H_2 uptakes in the type-I and the linear H_2 adsorption isotherms

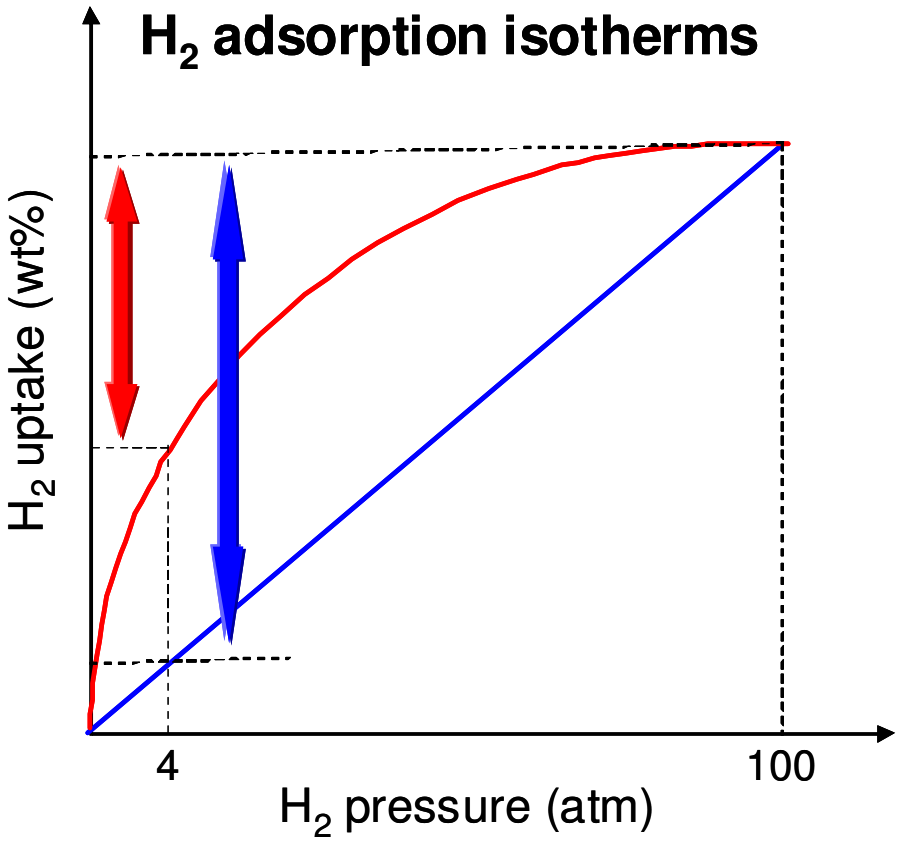

Figure S4. Comparison of delivery H_2 uptake in the type-I H_2 adsorption isotherm (red) versus the linear isotherm (blue). Here, the delivery H_2 uptake is shown with red (for type I) and blue (linear) arrows, indicating that the linear H_2 adsorption isotherm shows higher delivery H_2 uptake than the type-I.

S.6 Volumetric delivery H_2 uptake

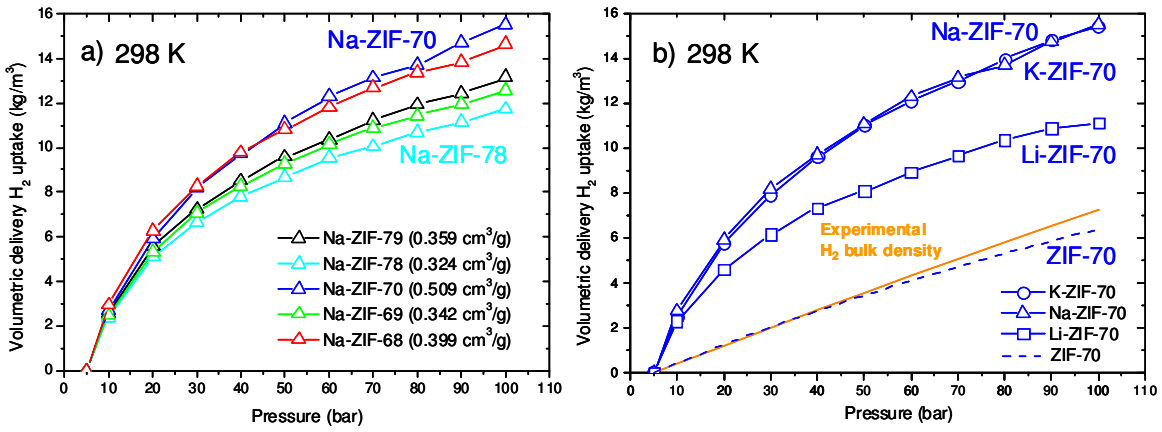

Figure S5. (a) Volumetric delivery H_2 uptake of Na-doped ZIFs at 298 K, and (b) volumetric delivery H_2 uptake of alkali metal-doped ZIF-70 at 298 K, where pristine ZIF-70 and experimental H_2 bulk density are also included for comparison.

Figure S5(a) shows the effect of free volume on the volumetric delivery H_2 uptake capacity in Na-doped ZIFs at 298 K. Similar to gravimetric delivery H_2 uptake, the larger free volume of ZIFs leads to the higher volumetric delivery H_2 uptake. For example, the delivery H_2 uptake order is

Na-ZIF-70 (15.50 kg/m^3) > Na-ZIF-68 (14.62 kg/m^3) > Na-ZIF-79 (13.14 kg/m^3) > Na-ZIF-69 (12.57 kg/m^3) > Na-ZIF-78 (11.73 kg/m^3),

which correlates with the order of their free volumes:

Na-ZIF-70 (0.509 cm^3/g) > Na-ZIF-68 (0.399 cm^3/g) > Na-ZIF-79 (0.359 cm^3/g) > Na-ZIF-69 (0.342 cm^3/g) > Na-ZIF-78 (0.324 cm^3/g).

Also, we shows volumetric delivery H_2 uptake of alkali metal-doped ZIF-70 at 298 K in Fig. S5(b). Alkali metal ion dopants improve volumetric H_2 uptake capacity at 298 K and the volumetric uptake order is Na-ZIF-70 (15.50 kg/m^3) > K-ZIF-70 (15.40 kg/m^3) > Li-ZIF-70 (11.11 kg/m^3) > ZIF-70 (6.38 kg/m^3). Similar to the gravimetric delivery uptake case, higher H_2 binding energy

needs not always lead to higher delivery H_2 uptake. And, although pristine ZIF-70 shows lower volumetric delivery H_2 uptake than experimental H_2 bulk density, alkali metal-doped ZIF-70 have higher volumetric uptake than the experimental H_2 bulk density, indicating that the alkali metal-doped ZIFs is more efficient than the compressed gas tank for hydrogen storage.

S.7 References

S1. Q-CHEM software (Version 3.2, Q-Chem Inc., Pittsburgh)

S2. Kittel, C. *Introduction to Solid State Physics 7th Edition*, John Wiley & Sons, Inc.

S3. Han, S. S.; Choi, S.-H.; Goddard, W. A. III *J. Phys. Chem. C* **2010**, *114*, 12039